§171.1(c)(H)

00F - 1487

EA 2

§171.1(c)(H)   ENVIRONMENTAL ASSESSMENT

Section Contents

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4 DESCRIPTION OF THE PROPOSED ACTION

4.1 REQUESTED APPROVAL

Approval is requested for the use of the system comprised of acidified sodium chlorite (ASC) solutions for post-chill use as an antimicrobial agent to reduce pathogenic microorganisms on the cut surfaces of poultry meat, organs, and related poultry parts or trim for use as such, or prior to their being ground into chopped meat and related comminuted products. The petitioned additive was originally approved as a Secondary Direct Food Additive (FAP 4A4433) on April 23, 1996. New regulation 21CFR §173.325 was codified to reflect the acceptance of ASC for use as an antimicrobial agent in the processing of poultry meat as a component of a carcass spray or dip solution prior to immersion in pre-chiller or chiller waters, or for direct application in pre-chiller or chiller water solutions. Further approvals for the additive have been granted in the intervening period. As of the date of submission of the current FAP, the approved applications for acidified sodium chlorite on poultry meat were most recently codified and/or listed in the Federal Register on March 28, 2000. A copy of this listing follows:

173.325   Acidified Sodium Chlorite Solutions.

(b) (1) The additive is used as an antimicrobial agent in poultry processing water in accordance with current industry practice under the following conditions:

    (i)   As a component of a carcass spray or dip solution prior to the immersion of the intact carcass in a prechiller or chiller tank;

    (ii)   In a prechiller or chiller solution for application to the intact carcass;

    (iii)   As a component of a spray or dip solution for application to poultry carcass parts; or

    (iv)   In a prechiller or chiller solution for application to poultry carcass parts.

    (2)   When used in a spray or dip solution, the additive is used at levels

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that result in sodium chlorite concentrations between 500 and 1200 parts per million (ppm), in combination with any GRAS acid at a level sufficient to achieve a solution pH of 2.3 to 2.9.

(3) When used in a prechiller or chiller solution, the additive is used at levels that result in sodium chlorite concentrations between 50 and 150 ppm, in combination with any GRAS acid at levels sufficient to achieve a solution pH of 2.8 to 3.2.

US Department of Agriculture (USDA) interim approval for the use of ASC solutions on Poultry Meat was also granted on January 7th, 1999 as a consequence of a petition submitted by Alcide Corporation to amend 9 CFR 381.147(f)(4). Final rule making to amend 9 CFR 381.147(f)(4) is in process at the time of writing of the current petition.

In ASC solutions, there are two components that are used to create the antimicrobial effect, the food-grade acid and the sodium chlorite. Sufficient acid is added to a 500 - 1,200 parts per million (ppm) solution to reduce its pH to the 2.3 - 2.9 range. The resulting ASC solutions are then applied to the poultry meat surfaces as either a spray or a dip. In the former case, the liquid is dispensed from a spray apparatus in which either:

i) Two streams of the chlorite and the acid solutions are mixed at, or immediately before the spray nozzle, or;

ii) A single stream of ASC solution is directed to the spray nozzle from a pre-mixed solution. The latter may be prepared up to 8-hours prior to spraying, preferably in cold water, so long as the chlorite and acid levels have been analytically determined to be within acceptable levels.

When the antimicrobial solution is applied as a dip, the meat pieces are immersed in the dip solution for a brief period of time, generally 10 to 30 seconds.

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4.2   NEED FOR THE ACTION

Millions of Americans become ill each year from something they eat. While diagnostic and surveillance methods for food borne illness have improved dramatically in recent years, the exact number of cases can still only be approximated by government officials. As a result we must rely heavily on estimates when attempting to quantify the problem. As an example, the Centers for Disease Control and Prevention estimates that while deaths due to food poisoning have dropped from 9,000 to 5,000 per year, the actual number of illness' reported has risen to approximately 76 million per year. Much of this increase is attributed to better surveillance and more accurate diagnosis. 30% of the reported food poisonings are also now known to be bacterial in origin, arising mainly from infections due to *Campylobacter jejuni, Salmonella spp.* and *Shigella spp.*

There is therefore a strong need for good hygienic practices after the initial post-slaughter (pre-chill) decontamination of poultry meat carcasses, in order to ensure the unbroken microbiological safety and quality of secondary cuts, retail meat cuts and specialty meats that are derived from post-chill carcasses during the further processing phase of carcass cutup. Of particular importance are the "ready to eat" and comminuted poultry meat products, in which pathogenic organisms such as *Listeria monocytogenes* can re-contaminate during further processing and may become intimately combined with the finished product. Unless proper temperatures are achieved during the cooking of the finished poultry meat product to destroy such pathogens, they can survive and cause illness or even death to the consumer. *Listeria monocytogenes* is widespread in the environment and in certain foods. Control efforts can reduce the incidence of Listeria in the environment and, if combined with a strict intervention program to control pathogenic organisms in the food plant, it should be possible to minimize ready to eat product contamination with this organism.

Other pathogens may also be recovered from post-chill poultry meats, organs and related parts or trim in meat-handling facilities where good hygiene is not always

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sufficient to eliminate them completely. These pathogens, include various *Salmonella* species, *Staphylococcus aureus* and *Campylobacter jejuni*. These pathogens also require additional means (intervention steps) to diminish or eliminate their numbers than just the customary surface rinsing with chlorinated water which poultry meat pieces typically sustain.

It is the position of the Alcide Corporation that the ASC solutions which are the subject of this Food Additive Petition, and which have already been approved by the FDA for use in both poultry carcass and red meat carcass processing (pre-chill), as well as red meat carcass parts and organs processing (post-chill), can play a major role in upgrading the microbial quality of primary and secondary poultry meat cuts, organs and related meat parts and trim. In addition, the use of ASC solutions on poultry meat post-chill would further enhance the microbial quality of those materials, which are destined for further processing to ultimately end up in the U.S. ground meat supply.

4.3 LOCATIONS WHERE PRODUCTS WILL BE PRODUCED

There are two components to the acidified chlorite solutions being proposed for Secondary Direct Food Additive Status, the sodium chlorite or Base component, and the acidifier or Activator component needed to achieve the desired solution pH. The acidifier can be any one of a variety of FDA-approved GRAS acids, including phosphoric, sulfuric, malic, acetic and citric. These are all materials of very high volume usage, and of many current and diverse applications in a wide variety of industries around the US today. The projected volumes of use of any of these acids as an activator of sodium chlorite to generate an ASC solution are much below a fractional percentage of the other applications. Thus the sites of production of these different acids, is not considered relevant to this environmental assessment.

Sodium chlorite is currently being used as a chlorine dioxide (ClO_2) source in water treatment, as well as an industrial bleaching agent in a number of industries

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(primarily pulp and paper), in cleaning applications for the electronics industry, as a biocide in the food processing industry, and in various applications in the oil industry. On April 23, 1996 the U.S. FDA first approved the use of sodium chlorite as a component of ASC solutions for microbial reduction pre-chill in poultry carcass sprays or dips and during the chill process as a component of the chill water. Thereafter, as a result of similar approval actions the FDA has also allowed for the use of ASC solutions; i) pre-chill in red meat carcass sprays or dips; ii) post-chill in red meat, red meat parts and organ sprays or dips; iii) pre-process on Raw Agricultural Commodities; iv) in process waters on sea food.

The size of the North American market in 1992 was estimated at 18 million lb. per year, and with a demand for chlorite growing (at the expense of chlorine) at a rate of 8% to 9% per year, reached approximately 25 million lb. per year by 1996[a]. In the early 1990's, the major production source was Olin Chemical's 13.5 million lb. per year Niagara Falls manufacturing site. Today this product is marketed by Vulcan Chemicals, Birmingham, Alabama. Vulcan's new 18 million lb. per year facility in Wichita, Kansas will result in the closing of the Niagara Falls plant. Sterling Chemicals, of Houston, Texas has also acquired Tenneco's production facility in Richmond, Virginia, to add to its 8 million lb. per year sodium chlorite manufacturing plant in Buckingham, Quebec. Foreign production sites for sodium chlorite, which may be accessed if quality and economics are appropriate, include that of France's Atochem, S.A., the world's largest producer, and Energia Industrias Aragonesas, Madrid, Spain.

4.4   LOCATIONS WHERE THE PRODUCTS WILL BE USED

Once the pending FAP is accepted as a modification of the current regulation, the ASC antimicrobial solution will become available to all poultry processors, an increasing number of which are now carrying out whole carcass disinfection with the ASC solutions

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(a) Resurgence in Demand Reviving Market for Sodium Chlorite", in Chemical and Engineering News, p. 11,12 March 22, 1993.

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(*ca.* 6% of all US plants, as of this writing). A generalized overview of poultry processing sites can be obtained by reference to the " Broiler Industry" year-end industry report for 1998, and which has not changed appreciably since that time. Of the 54 U.S. broiler companies surveyed, the range of percentages of total production was from 25.0% (for No. 1 ranked Tyson Foods, Inc.) to 0.10% (for lowest ranking). The following survey data is useful in identifying where the ASC antimicrobial solutions will find application.

- The largest four companies had 54.5% of the volume; this was accomplished in 80 primary slaughter plants and 28 further processing plants.
- The largest 19 companies had 91% of the volume; this was accomplished in 134 primary slaughter plants and 49 further processing plants.

The names, and base of operation of the 19 largest broiler processors are provided below together with the number of slaughter plants and further processing plants that are operated by each company.

	Company	Slaughter Plants	Further Proc. Plants
1)	Tyson Foods, Inc., Springdale, Arkansas	43	19
2)	Perdue Farms, Inc., Salisbury, Maryland	13	3
3)	Gold Kist, Inc., Atlanta, Georgia	12	
4)	ConAgra, Inc. , Omaha, Nebraska	12	6
5)	Pilgrims's Pride Corp., Pittsburgh, Texas	9	1
6)	Wayne Poultry Divn. Continental Grain, Inc, Duluth, Georgia	8	3
7)	Foster Farms, Livingston, California	5	2
8)	Sanderson Farms, Inc. Laurel, Mississippi	5	1

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9)	Cagle's Inc., Atlanta, Georgia	4	3
10)	Wampler-Longacre Chicken, Inc., Hinton, Virginia	4	
11)	Townsends, Inc., Millsboro, Delaware	3	1
12)	Fieldale Farms, Inc., Baldwin, Georgia	3	1
13)	Allen Family Foods, Inc., Seaford, Delaware	3	
14)	Marshall Durbin Cos.,	3	
15)	Simmons Foods, Inc., Siloam Springs, Arkansas	3	3
16)	Mountaire Farms, Inc.,	3	
17)	Peco Foods, Inc.,	3	1
18)	OK Foods, Inc., Siloam Springs, Arkansas	2	5
19)	Choctaw Maid Farms, Inc.	2	

The remaining 9% of the annual slaughter (nine poultry companies) is carried out in an additional 14 slaughter plants with further processing in an additional 10 plants.

Turkey processors are located in the same general areas as the chicken processors, and often are components of the above companies. For example, Conagra (#4), Foster Farms (#5), Wampler-Longacre (#10) and Simmons Foods (#15) have significant turkey processing facilities. It is anticipated that a disproportionately large share of turkey processors will be opting for use of the ASC solutions on excised, external poultry parts, rather than applying them to the full carcasses. To the extent that such application will be made to excised, pre-chiller turkey parts rather than to the full carcasses, such use would lower the anticipated ASC volume of use.

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5 IDENTIFICATION OF CHEMICAL SUBSTANCES THAT ARE THE SUBJECT OF THE PROPOSED ACTION

5.1 CHEMICAL NAMES AND PHYSICAL PROPERTIES

5.1.1 Sodium Chlorite

CAS Reg. No.:	7758-19-2
Color (37% Solution):	Colorless to light green
Specific Gravity:	1.21
Viscosity (@25°C):	1.62 cps
pH:	12.33

5.1.2 Acidifiers (GRAS)

Phosphoric Acid

CAS Reg. No.:   7664-38-2

Conforms with 21CFR §182.1073 as a Multiple Purpose GRAS Food Substance

Citric Acid

CAS Reg. No.:   77-92-9 (anhydrous)

5949-29-1 (monohydrate)

Conforms with 21CFR §182.1033 as a Multiple Purpose GRAS Food Substance

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Hydrochloric Acid

CAS Reg. No.:   7647-01-0

Conforms with 21CFR §182.1057 as Multiple Purpose GRAS Food Substance

Malic Acid

CAS Reg. No.:   617-48-1 DL mixture

97-67-6   L isomer

Conforms with 21CFR §184.1069 as a Specific Substance Affirmed as GRAS, with respect to the following ¶'s,

        (a)   description

        (b)   specifications

        (c)   use as pH control agent

        (d)   maximum use level

Sulfuric Acid

CAS Reg. No.:   7664-93-9

Conforms with 21CFR §184.1095 as a Specific Substance Affirmed as GRAS, with respect to the following ¶'s,

        (a)   description

        (b)   specifications

        (c)   use as pH control agent

        (d)   maximum use level

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Acetic Acid

CAS Reg. No.:   64-19-7

Conforms with 21CFR §184.1005 as a Specific Substance Affirmed as
GRAS, with respect to the following ¶'s,

      (a)   description

      (b)   specifications

      (c)   use as a pH control agent

      (d)   maximum use level

5.2 MODE OF ACTION OF THE GERMICIDAL SYSTEM

Acidified Sodium Chlorite (ASC) chemistry is principally the chemistry of chlorous acid ($HClO_2$; CAS No. 13898-47-0), a metastable oxychlorine species which decomposes to form chlorate ion, chlorine dioxide, and chloride ion[1]. To better understand chlorous acid chemistry, a brief overview of the chemistry of various oxychlorine species will be given.

As illustrated in Table I, chlorine can exhibit oxidation states from –1 to +7. As a consequence, its chemistry is varied and complex.

Table 1. Oxidation States of Chlorine

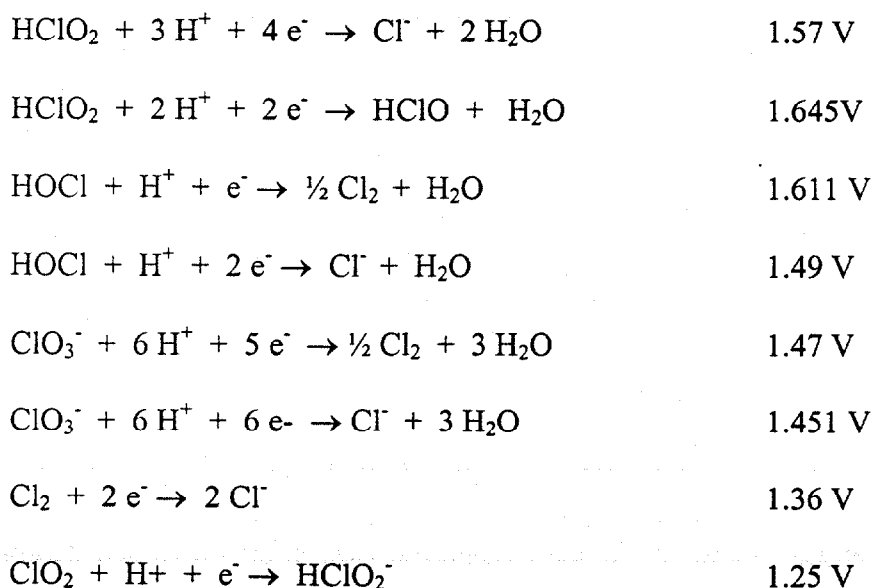|		
ClO_4^-	+7	Perchlorate ion
ClO_3^-	+5	Chlorate ion
ClO_2	+4	Chlorine dioxide
ClO_2^-	+3	Chlorite ion
ClO^- or OCl^-	+1	Hypochlorite ion
Cl_2	0	Chlorine
Cl^-	-1	Chloride ion

Oxychlorine species are important as oxidants in a number of applications. The strength of an oxidant is measured by its oxidation strength, or oxidation potential. Table 2 lists some of the more common oxidants, the associated oxidation reaction, the oxidation strength (measured in volts),
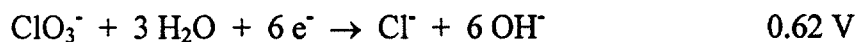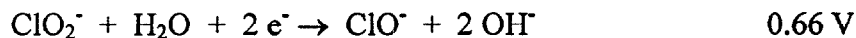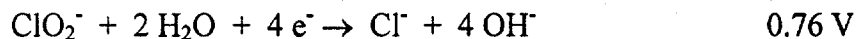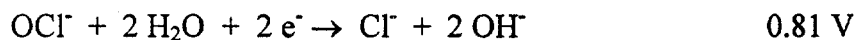
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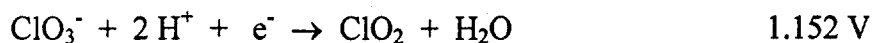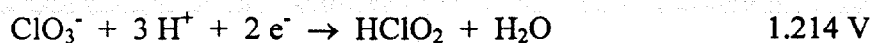
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and the oxidation capacity (the number of electrons accepted by the oxidant. The chlorous acid ($HClO_2$) reaction, with its 1.57 V oxidation strength and 4-electron oxidation capacity, ranks just below ozone and the hydroxyl-radical generation reaction of hydrogen peroxide.
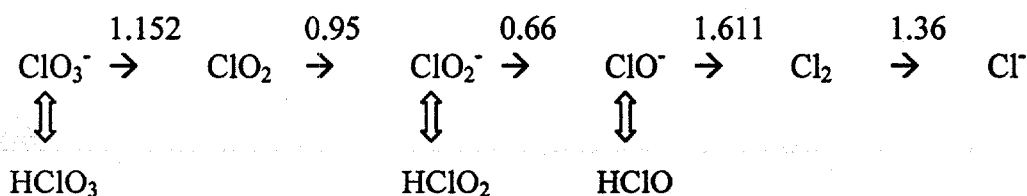
Table 2. Common Oxidation Reactions

Oxidant Reaction	Common Name	Oxidation Capacity	Oxidation Strength (V)
$O_3 + H_2O + 2\,e^- \rightarrow O_2 + OH^-$	Ozone	$2e^-$	2.07
$H_2O_2 + 2e^- \rightarrow 2\,OH^-$	Hydrogen Peroxide	$2e^-$	1.78
$HClO_2 + 3\,H^+ + 4\,e^- \rightarrow Cl^- + 2\,H_2O$	Chlorous Acid (Acidified Sodium Chlorite)	$4e^-$	1.57
$ClO_2\,(v) + e^- \rightarrow ClO_2^-$	Chlorine Dioxide (Vapor Phase)	$1e^-$	1.56
$HOCl + H^+ + 2\,e^- \rightarrow Cl^- + H_2O$	Hypochlorous acid	$2e^-$	1.49
$HOBr + H^+ + 2\,e^- \rightarrow Br^- + H_2O$	Hypobromous acid	$2e^-$	1.33
$ClO_2 + 4\,H^+ + 5\,e^- \rightarrow Cl^- + 2\,H_2O$	Acidified Chlorine Dioxide	$5e^-$	1.51
$ClO_2\,(aq) + e^- \rightarrow ClO_2^-$	Chlorine Dioxide (Aqueous Phase)	$1e^-$	0.95
$ClO_2^- + 2H_2O + 4e^- \rightarrow Cl^- + 4\,OH^-$	Chlorite	$4e^-$	0.78

As mentioned before, oxychlorine chemistry is varied and complex. Listed below are oxidation half-cell reactions and their corresponding oxidation potentials for several additional reactions of oxychlorine species given by Gordon et al.[2], in the AWWA publication, *Disinfectant Residual Measurement Methods*:

$$HClO_2 + 3\,H^+ + 4\,e^- \rightarrow Cl^- + 2\,H_2O \qquad 1.57\ V$$

$$HClO_2 + 2\,H^+ + 2\,e^- \rightarrow HClO + H_2O \qquad 1.645 V$$

$$HOCl + H^+ + e^- \rightarrow \tfrac{1}{2}\,Cl_2 + H_2O \qquad 1.611\ V$$

$$HOCl + H^+ + 2\,e^- \rightarrow Cl^- + H_2O \qquad 1.49\ V$$

$$ClO_3^- + 6\,H^+ + 5\,e^- \rightarrow \tfrac{1}{2}\,Cl_2 + 3\,H_2O \qquad 1.47\ V$$

$$ClO_3^- + 6\,H^+ + 6\,e\text{-} \rightarrow Cl^- + 3\,H_2O \qquad 1.451\ V$$

$$Cl_2 + 2\,e^- \rightarrow 2\,Cl^- \qquad 1.36\ V$$

$$ClO_2 + H+ + e^- \rightarrow HClO_2^- \qquad 1.25\ V$$

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$$ClO_3^- + 3\,H^+ + 2\,e^- \rightarrow HClO_2 + H_2O \qquad 1.214\ V$$

$$ClO_3^- + 2\,H^+ + e^- \rightarrow ClO_2 + H_2O \qquad 1.152\ V$$

$$ClO_2 + e^- \rightarrow ClO_2^- \qquad 0.95\ V$$

$$OCl^- + 2\,H_2O + 2\,e^- \rightarrow Cl^- + 2\,OH^- \qquad 0.81\ V$$

$$ClO_2^- + 2\,H_2O + 4\,e^- \rightarrow Cl^- + 4\,OH^- \qquad 0.76\ V$$

$$ClO_2^- + H_2O + 2\,e^- \rightarrow ClO^- + 2\,OH^- \qquad 0.66\ V$$

$$ClO_3^- + 3\,H_2O + 6\,e^- \rightarrow Cl^- + 6\,OH^- \qquad 0.62\ V$$

The oxidation potential diagram given below shows that chlorous acid is unstable with respect to disproportionation, i.e. chlorous acid is a metastable species.

$$
\begin{array}{ccccccccccc}
& 1.152 & & 0.95 & & 0.66 & & 1.611 & & 1.36 & \\
ClO_3^- & \rightarrow & ClO_2 & \rightarrow & ClO_2^- & \rightarrow & ClO^- & \rightarrow & Cl_2 & \rightarrow & Cl^- \\
\Updownarrow & & & & \Updownarrow & & \Updownarrow & & & & \\
HClO_3 & & & & HClO_2 & & HClO & & & &
\end{array}
$$

Numerous researchers have determined that the decomposition reaction of chlorous acid is approximately second order with respect to chlorous acid[3,4,5,6]. At pH values above 2.0 where $[ClO_2^-] > [HClO_2]$, the rate law can be written as follows:

$$\frac{-d[HClO_2]}{dt} = k\,[HClO_2]^2$$

(where $k = 0.023\ M^{-1}\ sec^{-1}$ at $25^\circ C$)[7]

It is known that chloride ion accelerates the decomposition of chlorous acid and also alters the stoichiometry. Hong[8,9] developed the following empirical rate expression for the decomposition of chlorous acid, with the effect of chloride taken into account;

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$$\frac{d[ClO_2]}{dt} = (m + nx)\left(1 - \frac{x}{p + qx}\right)$$

where $\quad m = 2\{k_1[HClO_2]^2 + k_2[ClO_2^-][HClO_2]\}$

$n = 4k_5[H+][HClO_2]$

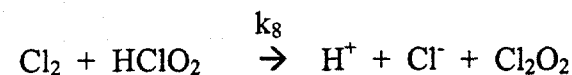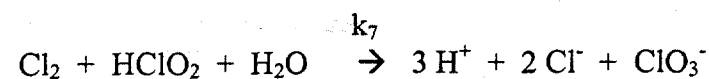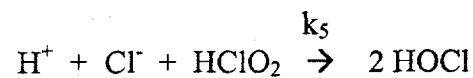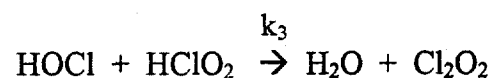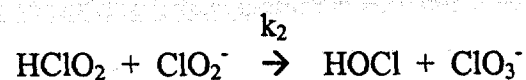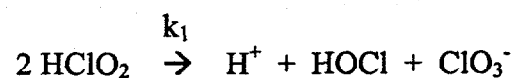$$p = \frac{k_3(k_7 + k_8)[HClO_2]}{k_6k_7[H^+]}$$

$$q = \frac{k_7 + k_8}{k_7}$$

$x = [Cl^-]$

(Where the various rate constants refer to the following set of reactions:)

$$2\,HClO_2 \xrightarrow{k_1} H^+ + HOCl + ClO_3^-$$

$$HClO_2 + ClO_2^- \xrightarrow{k_2} HOCl + ClO_3^-$$

$$HOCl + HClO_2 \xrightarrow{k_3} H_2O + Cl_2O_2$$

$$Cl_2O_2 + HClO_2 \xrightarrow{k_4} H^+ + Cl^- + 2\,ClO_2$$

$$H^+ + Cl^- + HClO_2 \xrightarrow{k_5} 2\,HOCl$$

$$H^+ + Cl^- + HOCl \xrightarrow{k_6} Cl_2 + H_2O$$

$$Cl_2 + HClO_2 + H_2O \xrightarrow{k_7} 3\,H^+ + 2\,Cl^- + ClO_3^-$$

$$Cl_2 + HClO_2 \xrightarrow{k_8} H^+ + Cl^- + Cl_2O_2$$

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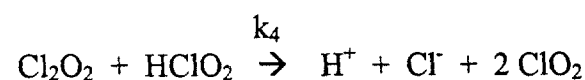
In the absence of chloride, only the first four reactions need be considered. Doing this, Hong gives the following reaction equation, valid over the pH range of 0 to 3, for the initial rate law for the formation of chlorine dioxide:

$$\frac{d[ClO_2]}{dt} = k\,[HClO_2]^2 + k'\,[HClO_2][ClO_2^-]$$

The rate of formation of chlorine dioxide given above can be related approximately to the disappearance of chlorous acid by the following relation[5]:

$$-d[HClO_2]/4 = d[ClO_2]/2$$

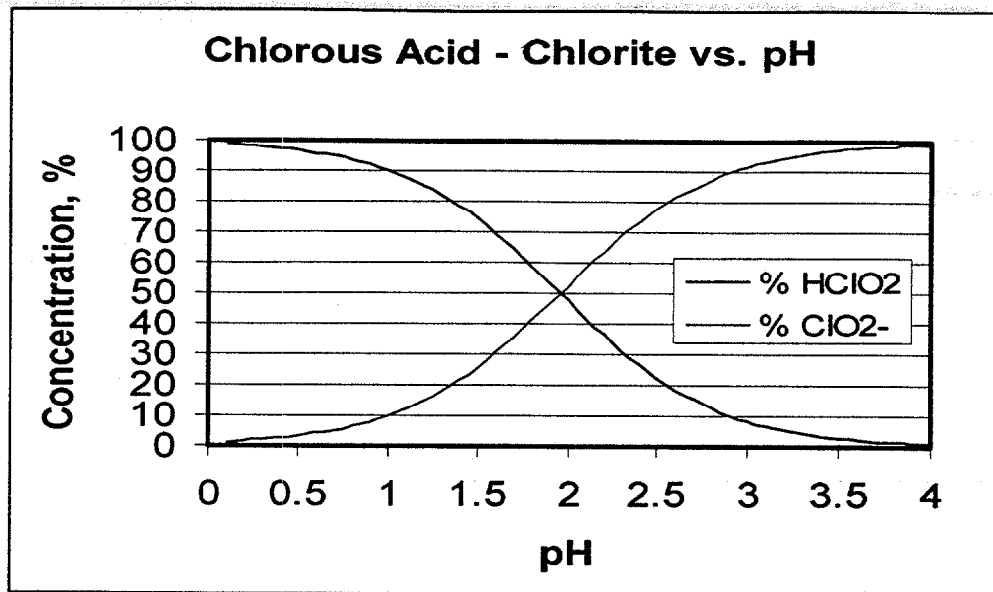In aqueous solution, chlorous acid, a relatively weak acid, dissociates as follows:

$$HClO_2 \quad \overset{K_a}{\Leftrightarrow} \quad H^+ + ClO_2^-$$
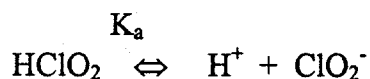
Where K_a, the acid dissociation constant, is 1.01×10^{-2} at 23°C[10]. In terms of the acid dissociation constant (ionization constant) and the hydrogen ion concentration of the solution (=10-pH), the chlorous acid concentration can be found from the total titratable chlorite concentration as follows:

$$\% \; HClO_2 \quad = \quad \frac{1}{1 + (1.1 \times 10^{-2})/[H^+]} \; \times \; 100\%$$

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The following is a graph of this relationship.

Chlorous Acid - Chlorite vs. pH

Based on the above theoretical, empirical and published understanding of the basic chemistry plus accumulated data relating to dose optimization, the optimal parameters for application of the Acidified Sodium Chlorite process as a short-term antimicrobial intervention have therefore been determined to be:

i)   A pH range of approximately 2.3 to 2.9;

ii)   A sodium chlorite concentration ranging from 500 ppm to 1200 ppm.

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6 INTRODUCTION OF SUBSTANCES INTO THE ENVIRONMENT

6.1 PRODUCTION RELEASES

As noted in Section 4, the ASC solution will be produced on site some time prior to application in the processing facility, be it a major operation, a contract operation for a specific chain, or ultimately even a supermarket facility. The solution mixing will take place through the confluence of the separate acid activator and sodium chlorite solutions at some point prior to the final applicator nozzles. The acid and sodium chlorite solutions will be prepared in ambient temperature tap water. During the typically brief time (no greater than 2 – 3 minutes) that will normally elapse between the creation/activation of the ASC solution and its final delivery to the surface to be treated, the levels of dissolved chlorine dioxide that are typically generated within the ASC solution will not exceed *ca.* 1 – 2 mg/liter (1 – 2 ppm).

In larger operations, it is anticipated that a spray treatment is most likely to be the primary mode of application to products which are the subject of this petition, in essentially the same manner as is currently commercially utilized for the pre-chill ASC treatment of whole poultry carcasses or carcass parts; i.e. they will pass through a semi-enclosed and baffled spray enclosure. The spray will be applied via pressurized spray nozzles, for varying exposure times up to about 30 seconds before the product exits the enclosure. In order to minimize the potential for possible off-gassing into the immediate worker environment, the semi-enclosed spray enclosure will be negatively pressurized via an aspirating air hose venting to the outside of the building. This will ensure the removal of excess gaseous materials, while a dedicated drainpipe will route excess fluids to an enclosed drain for removal with other plant wastes. Short term exposure, immersion dip processes may also be developed for the products that are the subject of this petition and, as for the spray treatments, such systems would also be semi-enclosed and negatively pressurized via an aspirating air hose venting to the outside of the building.

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In smaller operations where the application of product is expected to typically be limited to infrequent and/or small batch application using hand-held "on/off-type" applicators, the volume of product use and therefore the potential for off-gassing and worker environment exposure is significantly reduced compared to the larger commercial systems. As a result, no special precautions other than the inclusion of label precautionary statements regarding handling and use of the material are therefore anticipated.

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6.1.a. THEORETICAL WORSE CASE PRODUCTION RELEASES

While chlorine dioxide has a minimum tendency to form in ASC solutions when, the chlorite and acid are initially combined immediately prior to spraying (typically measured as < 1 – 2 mg/liter dissolved in solution), it may exhibit an increasing tendency to form as the applied solution concentrates during the evaporative process. Thus, in a typical situation, the potential for chlorine dioxide entry into the air of the workplace would be expected to derive primarily from this evaporative source, more so than from that which is retained in solution. Chlorine dioxide also has a significant tendency to react with, and be degraded by soluble organic matter (such as blood proteins) to chlorite and ultimately chloride. It is therefore expected that a major portion of both the initially projected chlorine dioxide maximum of 1 – 2 mg/liter in solution and any quantity formed upon subsequent solution evaporation will be reduced to a non-volatile, chlorine-containing ion that will be removed in the organic matter laden waters of the processing plant.

Finally, it is further expected that the degree of chlorine dioxide evolution out of the ASC solution within the application enclosure during the treatment's 30-second residence time on the poultry meat pieces will be low. This is particularly true because the high humidity conditions prevailing in the cabinet will tend to suppress evaporation and therefore out-gasing of chlorine dioxide from the ASC solution. Thus the 1 – 2 mg/liter level of chlorine dioxide that can typically be measured in an ASC solution within 2 – 3 minutes of activation of sodium chlorite can be assumed to correspond to the most likely "maximum" amount of this substance that will arise from both initial and evaporative sources.

To put this into perspective, a typical ASC spray operation in a commercial poultry plant applies 150 ml of ASC solution per 3 pound of meat (one average sized carcass) inside of a 2.44M^3 spray enclosure over the course of 15.9 seconds.[b] Therefore in a "worst case" scenario

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(b) For a standard 90 bird per minute evisceration line a typical Sanova spray cabinet enclosure measures 3(0.67M x 1M x 1.22M). Therefore internal volume = 2.01 M^3. Average carcass exposure time to ASC chemistry while transiting the spray cabinet = cabinet length (3.66 M)/Line Speed. Line Speed = No. birds per second x shackle width = 90/60 x 0.15M. Therefore transit time = 3.66/0.23 = 15.9 seconds

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where all of the dissolved chlorine dioxide were to be released into the environment, 1,000 pounds of meat treated (333 carcasses), corresponding to 50 liters of ASC solution applied, would release 100 mg of chlorine dioxide in 3.70 minutes (at the 2 mg/liter concentration).[c] Assuming a static air environment inside the application enclosure, with no venting or circulation of the air in the vicinity of the treated poultry meat, the dispersal of up to 10 mg of chlorine dioxide into 2.44 M^3 of air would rapidly raise its concentration above the OSHA 8-hour TLV of 0.3 mg/M^3 and therefore lead to unsafe conditions both within the enclosure and in the immediate external environs.

6.1.b. ACTUAL PRODUCTION RELEASES

Air quality testing in the immediate area around commercial spray enclosures installed into poultry plants in the US shows that chlorine dioxide is generally undetectable (Appendix 2). Additionally, air quality testing of the air exhaust from these same commercial systems shows extremely low levels of chlorine dioxide present, further supporting the fact that the majority of the material that is in solution remains so and is ultimately disposed of in the liquid waste stream.

In an immersion or dipping operation there is not expected to be any change, certainly no increase to the potential for air dispersal of either the ASC solution or of any dissolved chlorine dioxide, when compared to that of a spray operation. As with the Sanova commercial spray systems, the environs surrounding an immersion or dipping operation will be controlled with appropriate enclosures, containment of liquid wastes and positive pressure air venting.

(c) 1000 lb meat = 333 carcasses. At 90 birds per minute line speed 333 carcasses = 3.72 minutes of kill time. 1000 lb meat x 150 ml/3 lb x 1 L/1000 mL = 50 L.

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6.2 USE RELEASES

6.2.1 ESTIMATES OF RAW MATERIAL VOLUME

6.2.1.a INTRODUCTION

Data on the exact amount of poultry meat that is further processed beyond whole carcass is difficult to obtain in the US since actual industry practices vary widely due to market demand and changes in the market interest. From a survey conducted by Alcide Corporation amongst USDA Marketing Services, Poultry Industry and Poultry Association personnel, the following approximate numbers were obtained.

For the top 43 poultry processors:

- 72.5% of product is marketed as fresh product, 25% is marketed as frozen product. (Fresh and frozen includes whole birds, cutup and tray pack).
- 73.4% of whole carcasses go to cutup and de-bone.
    - De-bone is mainly of breasts and thighs.
    - Cutup encompasses split breasts, de-boned breasts, thighs, leg quarters, drums and thighs, wings.
- Of the carcasses going to cutup and de-bone, 32% is processed as value-added. This includes formulated products, portioned and formed products, cooked, canned and pre-browned products, sausages and frankfurters, deli items.
- Estimates of the ratios for the processing of turkey meats indicate that these are about the same as those for chickens.

These ratios together with actual application rates for the Sanova® system as currently commercialized in poultry plants in the US can be applied to the available production statistics for the poultry industry to obtain theoretical estimates of the potential usage rates for sodium chlorite under various market share scenarios.

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6.2.1.b SODIUM CHLORITE ESTIMATES

In 1998 the USDA estimated that 28,386 million pounds of chicken and 5,281 million pounds of turkey were processed in the US therefore, assuming a "worse case" scenario where all of this poultry product is treated with ASC, the following are estimates of sodium chlorite usage:

Assumption 1: 100% of Carcasses Treated Pre-Chill	Chicken	Turkey	Total
Total Meat Processed in 1998			
(million lb)	28,386	5,281	33,667
(million Kg)	12,876	2,395	15,271
Treatment Volume (rate = 110 ml/Kg)			
(million L)	1,416	263	1,680
Chlorite Use (rate = 1.2 gm/L)			
(million Kg)	1.70	0.32	2.02

Assumption 2: 73.4% of Carcasses Re-Treated Post-Chill	Chicken	Turkey	Total
Total Meat Processed in 1998			
(million Kg)	9,451	1,758	11,209
Treatment Volume (rate = 110 ml/Kg)			
(million L)	1,040	193	1,233
Chlorite use (rate = 1.2 gm/L)			
(million Kg)	1.25	0.23	1.48

Therefore, in this worse case scenario assuming that all poultry meats were to receive both a pre-chill and a post-chill exposure to an ASC treatment, the total sodium chlorite usage per annum is estimated to be circa. 2.02 + 1.48 million Kg, = 3.5 million Kg or 30.8% of the total sodium chlorite market in the US (estimated at 11.35 million Kg in 1996). Clearly this number is highly inflated and does not reflect a realistic picture of the industry's likely adoption of the ASC

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technology for pre-chill and/or for post-chill use, or their likely use of alternative intervention technologies and the impact thereof. A more likely scenario is that ASC solutions might be expected to achieve a 20% share of the intervention technology market that is finally adopted by the poultry industry. For the post-chill treatment sector it is also estimated that 50% of the actual ASC product usage would be for single treatment only and the remaining 50% would be for combined pre- and post-chill treatment. Under this scenario, the projected total sodium chlorite usage per annum for both pre-chill and post-chill uses would be as follows:

Treatment	Pre-Chill	Post-Chill	Pre- & Post-Chill
Market Share	20%	10%	10%
Sodium Chlorite Use (million Kg)	0.404	0.148	$0.202^{\#} + 0.148$
Estimated Total Sodium Chlorite Usage (million Kg)			0.70

[#] Already accounted for in the Pre-Chill use numbers.

A total sodium chlorite usage rate of 0.70 million Kg therefore equates to circa 6.2% of the estimated current market for this material in the US.

6.2.2   WATER AND AIR RELEASES

6.2.2.a INTRODUCTION

The components of the ASC solutions are the GRAS acid, of high purity, and the sodium chlorite (of a technical grade), which has sodium chloride and sodium chlorate as impurities. Upon acidification the chlorite, through chlorous acid, can be expected to minimally transform to chlorine dioxide and to chlorate. At the level of use of these components, and the minimum standing time for the mixed ASC solution, the amount of chlorine dioxide that is dissolved in solution will not exceed *ca.* 1 –2 mg/liter. Being a highly reactive compound, this chlorine dioxide will quickly be reduced (by reaction with organic matter and with microorganisms on the

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meat surfaces) to even smaller quantities of chlorite and chloride ions. An even lower amount of chlorate will also be formed in this process by a separate pathway involving disproportionation of the chlorine dioxide.

As shown from plant data in previous Section 6.1, the air releases of chlorine dioxide are negligible. Of greater possible concern are the relatively higher levels of sodium chlorite, i.e. 1200 ppm as a maximum, of which the chlorite ion represents 895 ppm. As previously indicated, it is estimated that around 73% of post-chill carcasses go to cut-up or de-bone to end up as either fresh or frozen parts or as value added formed products. In the poultry industry, this further processing is typically carried out either as a secondary component of the slaughter operation in the same facility or in a separate, dedicated further processing facility, which acts as a central accumulation point for a number of slaughter operations.

6.2.2.b CHLORITE/CHLORATE/CHLORINE DIOXIDE WATER RELEASES - LARGER FACILITIES

A "worse case" estimate of the concentration of chlorite ion that might be discharged to Publicly Owned Treatment Works (POTWs), from ASC treatment of poultry carcasses pre-chill, can be approximated from the following assumptions:

- ASC product will typically be applied pre- and post-chill at the rate of 5 oz/3 lbs = 110 ml/Kg.
- At the optimal dose rate (1200 ppm), the amount of chlorite ion applied = 895 mg/L.
  - ➤ Therefore the amount of chlorite applied = 98.45 mg/Kg treated.
- Assuming 10% of the chlorite is consumed in reaction on the carcass surface, the residual chlorite entering the waste stream = 88.61 mg/Kg treated.
- Poultry processing plants generate an average of 6 gallons of waste-water per carcass processed = 16.7 L/Kg.
  - ➤ Therefore the amount of chlorite ion that could possibly enter the waste stream from pre-chill use = 88.81 mg/16.7L = 5.31 mg/L = 5.31 ppm.

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Using Alcide Corporation's estimates, the post-chill application of ASC on poultry meats would result in an additional 74% of the pre-chill amount attributable to sodium chlorite in the plant's POTW discharge.

> Therefore the incremental amount of chlorite ion that could possibly enter the waste stream from post-chill use = 3.93 ppm.
> The total amount of chlorite ion that could enter the waste stream from combined pre- and post-chill use = 9.24 ppm.

For sodium chlorate, a worse case estimate of the amount, which may be present, can be obtained from the following.

- Technical grade sodium chlorite, contains *ca.* 80%; pure material, and has no more than 4% sodium chlorate.
> Therefore at least initially, the ratio of chlorite to chlorate ion is ≥ 20:1.

Chloride ion is of no consequence, it being a small fraction (*ca.* 0.1) of the original chlorite, and a larger molar fraction (*ca.* ½) of the reacted chlorite on a weight basis. Chloride is also naturally present in such large quantities that any incremental amount arising from chlorite degradation is not going to be measurable.

Thus, the worse case levels of chlorite, chlorate and chlorine dioxide entering the POTWs from large scale processor use of ASC pre- and post-chill, based on the figures shown in the previous sections, are:

chlorite-	9.34 ppm
chlorate-	≤0.5 ppm
chlorine dioxide-	≤0.2 ppm

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It is important to remember that any contribution of industrial discharges to POTWs is further diluted by discharges from non-industrial sources. An approximation of the further dilution by these other sources can be made from information made available in an EPA- sponsored study by Consulting Engineers[11] of discharge sources which have a negative impact on the operation of POTWs. The POTWs studied included a representative cross-section of U.S. municipal treatment facilities serving industrial and non-commercial dischargers. In the 29 Case Study Reports provided in the survey, 26.3% of the influent wastewater to these facilities derived from industrial sources.

A single industrial discharge source to a particular POTW, such as a poultry processing plant, can be conservatively estimated to represent an upper limit of 50% of the total industrial discharge to a single POTW. Thus a water flow percentage contributed by a single poultry processor to a POTW is 26.3% x 50%, or 13.2% of the total water processed. On that basis the approximate maximum calculated chlorite, chlorate and chlorine dioxide levels, which might enter an average POTW would be:

chlorite;	9.34 ppm x 13.2% = 1233 ppb
chlorate;	≤ 0.5 ppm x 13.2% = ≤ 66 ppb
chlorine dioxide	≤ 0.2 ppm x 13.2% = ≤ 26 ppb

While the above estimated worst case value for chlorite exceeds the LC_{50} for Mysid Shrimp (refer to Section 8.1 of the Environmental Assessment of this petition), the oxidative tendency of this oxychlorine species to be chemically reduced by organic matter in both the processed-products treatment waters, plant sanitation waters, and subsequent municipal water treatment facilities, means that the final level of this material is expected to be de minimus and to be of no impact to aquatic species. For sodium chlorate, the estimated levels expected to be generated from a typical ASC application system are significantly below the >1000 ppm LC_{50} of freshwater and marine fish for this oxychlorine species. Finally, the rapidity of degradation, of chlorine dioxide in organic environments, eliminates this oxychlorine species from any consideration regarding aquatic toxicity. In aggregate, entry of the above levels of oxychlorine species in a POTW is therefore not expected to pose any risk towards aquatic species.

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6.2.2.c ACID IN WATER RELEASES – LARGER FACILITIES

With respect to the GRAS acids the following are representative of the levels required (buffering included) to acidify sodium chlorite to the petitioned pH range of 2.3 - 2.9:

sulfuric acid	≤0.005% (≤50 ppm)
phosphoric acid	0.01 - 0.02% (100 - 200 ppm)
citric acid	0.6 – 0.9%

These levels are clearly quite low, and like sodium chlorite, will be similarly diluted further by other water sources contributing to the facilities' effluents. Using the same assumptions as for chlorite[d] and assuming again that the water flow percentage contributed by a single poultry processor to a POTW is 26.3% x 50%, or 13.2% of the total water processed, the approximate maximum calculated sulfuric, phosphoric and citric acid levels, which might enter an average POTW would be:

sulfuric acid;	0.07 ppm
phosphoric acid;	0.27 ppm
citric acid;	12.25 ppm

6.2.2.d IMPACT OF WATER RELEASES – LARGER FACILITIES

Alcide Corporation does not believe that the above-indicated concentrations of oxychlorine species or food acids will have a negative impact on the operation of POTWs, for the following reasons:

1)   Neither chlorite, chlorate nor chlorine dioxide is listed as an Interfering

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(d) Application rate = 110 ml/kg, 10% of acid consumed in reaction, average 16.7L/kg waste water usage, post-chill application accounting for an additional 74% of the pre-chill usage

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Substance in POTWs, as provided in Page 125 of the Wetzel document[11]. These interfering substances, as contained in certain industrial discharges, can cause "a POTW's noncompliance with its permit or inability to lawfully use or dispose of its sludge." Chloride was listed as a potentially interfering substance, but at a level significantly higher (180 ppm) than its presence either as an impurity in the technical grade chlorite or if all the oxychlorines were converted to chloride. Acidity is also listed as a potential interference in POTW operation, but the levels contributed by this application would not have a measurable impact on pH.

2)   None of the species present at the levels indicated can interfere with the microbiological treatment systems. Chlorine dioxide, a recognized antimicrobial, will have no effect at the maximum ppb levels calculated; neither can the chlorite, a much weaker source of activity, at the 1233 ppb calculated.

3)   "Most interference problems at POTWs are related to intermittent discharges of high-strength conventional wastes which overload a POTW's organic capacity, causing plant upset," according to an EPA reporter[12]. The organic contribution of these systems is minimal, and the other common causes of plant interference are not a factor here:

> low pH .....[corrosion]
> solids or viscous pollutants.....[flow obstruction]
> high volatiles .....[explosion or fire hazard]
> heated discharges .....[altered biological activity]
> toxic discharges ..... [inhibited biological activity]

6.2.2.e WATER RELEASES – SMALLER FACILITIES

It is anticipated that most of the further processing of poultry carcasses in the US, up to 73%, will be produced in the larger facilities. The remaining ASC usage will be distributed over

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a wide range of local facilities of low volume production, thereby reducing the "per site" ASC volume.

Because of the diversity of such small-use operations the prediction of specific ASC quantities with respect to other waters in the effluent of a particular type of facility is not feasible. However it can be readily concluded that the much smaller chlorite and acid quantities in the facility's effluent would be at least as likely to react with and be degraded by the organic matter in its effluent water as in the larger facilities. Once again, the maximum level of oxychlorines (mostly chlorite) that might be expected in the plant effluent of a carcass operation is ~ 10 ppm. The same basic calculations with respect to impact on POTWs apply.

6.2.2.f AIR RELEASES – LARGER AND SMALLER FACILITIES

As seen earlier, based on the plant data from ASC application to whole carcasses, the spray application of an ASC solution to the cut surfaces of poultry meat, organs, and related poultry parts or trim creates negligible air levels of chlorine dioxide, in an environment of normal air turnover, assuming the use of an appropriately designed spray cabinet enclosure to confine its dispersal and to control the gaseous and liquid effluents.

In ASC immersion dip operations, where meat pieces will generally have some liquid exudate on their surfaces (in which soluble proteins will be contained) this organic matter is also expected to destroy any small levels of chlorine dioxide that may have formed in the solution upon its activation. In experiments in which pieces of poultry meat were, immersed in ASC dips solutions, there was no noticeable odor of chlorine dioxide above these solutions. The odor threshold for chlorine dioxide detectability is ~0.1 ppm[13]. The OSHA TLV for chlorine dioxide is also 0.1 ppm, for continuous 8-hour exposure[14]. As with the Sanova commercial spray systems, the environs surrounding an immersion or dipping operation will also be controlled with appropriate enclosures, containment of liquid wastes and positive pressure air venting.

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6.2.3. RELATION OF PLANT WATER RELEASES TO TOTAL PUBLICLY OWNED TREATMENT WORKS QUANTITIES

The industrial discharges to local Publicly Owned Treatment Works (POTWs), such as might be expected to occur from poultry slaughter facilities which secondarily process and treat the cut surfaces of poultry meat, organs, and related poultry parts or trim, are further diluted by discharges from other industrial and non-industrial sources. The previous section of this petition discussed the relationship of such plant discharges to total POTW intakes. Reference was made to an EPA-sponsored study,[15] that provided guidance in minimizing the discharge effects on these POTWs. In this report it was shown that the average influent waste-water from industrial sources was 26.3% of the total intake. That information was used to estimate the projected impact of the poultry meat-processing facilities using ASC treatments.

Based on the estimate that 74% of all poultry carcasses are destined for further processing (and therefore may potentially be exposed to a single (post-chill) or double pre-chill and post-chill) treatment with ASC, it can be presumed that the volume usage characteristics of the various primary and secondary poultry carcass processors that adopt a post-chill ASC treatment regime, will increase over those that were originally projected for a single pre-chill treatment (FAP 4A4433). Using Alcide Corporation's estimates of market share, the post-chill application of ASC on poultry meats would result in an overall increase of 74% in the POTW discharges attributable to sodium chlorite. As calculated in Section 6.2.2.a, the contribution from a carcass processor to its handling POTW is a maximum 1233 ppb.

A similar analogy holds for the food-grade acids used for ASC activation, where the acid contribution to POTW facilities would be *de minimus*.

On the basis of these discussions, Alcide corporation does not believe that the above-indicated concentrations of oxychlorine species or food acids will have a negative impact on the operation of POTW's, for the following reasons:

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a) The levels of oxychlorines, *i.e.,* chlorite, chlorate, and chlorine dioxide, that would reach the POTW's, is at the ppb level, at most. Neither chlorite, chlorate nor chlorine dioxide is listed as an Interfering Substance in POTWs, as provided in a document listing Interferences at POTWs[15]. These interfering substances, as contained in certain industrial discharges, can cause "a POTW's noncompliance with its permit or inability to lawfully use or dispose of its sludge." Acidity is also listed as a potential interference in POTW operation, but the levels contributed by this application would not have a measurable impact on pH.

b) None of the species present at the levels indicated can interfere with the microbiological treatment systems. Chlorine dioxide, a recognized antimicrobial, will have no effect at the calculated ppb level; neither will the chlorite, a much weaker source of activity, at the minuscule levels possibly present.

6.2.4 COMPLIANCE WITH EMISSION REQUIREMENTS

Alcide Corporation fully anticipates that any poultry slaughter operation that intends to use the ASC solutions, if deemed appropriate, will obtain the necessary permits and approvals for discharging process waters containing chlorite, chlorate and chlorine dioxide to POTWs. It should be noted that sodium chlorite, used in preparation of these ASC solutions, is an EPA-registered product. It is Alcide Corporation's current intention to use one of three EPA registered sodium chlorite products for the proposed application (or the equivalent): Vulcan Chemicals 79% Technical Sodium Chlorite, Technical Sodium Chlorite Solution 31.25, or 31% Active Sodium Chlorite Solution. Copies of the Technical Data Sheets and Material Safety Data Sheets for these products are provided in Appendix I of this section. Alcide Corporation intends to request that Vulcan Chemicals include label copy, which mandates that users of the sodium chlorite must discharge the solutions in accordance with the requirements of the facility's National Pollution Discharge Elimination System permit. Any warning statements on the labels concerning the hazard of the products to organisms that may be exposed to it in the environment will also be on the labels of the FDA-regulated use.

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6.2.5. COMPLIANCE STATUS

Sodium chlorite has a number of commercial uses, primarily as a source of chlorine dioxide, e.g., pulp and paper bleaching, drinking water treatment, as a slimicide in cooling towers, as a food disinfectant, and as a cleaning agent in the electronics industry. The current U.S. production of sodium chlorite is close to 25 million pounds (11.35 million Kg).

As shown in Section 6.2.1 of this petition, if all of the 8.0 billion chickens and 273 million turkeys processed in the U.S. per year were to be exposed to the maximum pre-chiller and post-chiller concentrations of ASC treatment, the total sodium chlorite consumed would be 3.5 million Kg. (Potentially, the use of ASC in the chiller tank could consume greater amounts of sodium chlorite, but this is considered to be an unlikely application option due to the very significant process control issues for this approach to treatment). On that basis a worse case maximum consumption of sodium chlorite per year for this application could not be expected to exceed 3.5 million lbs (30.8% of the total sodium chlorite consumed annually). However, Alcide Corporation's estimates of market share predict that the actual usage rates for sodium chlorite would be considerably less than this worse case scenario. More realistically it can be postulated that actual use rates would not exceed 0.70 million Kg per annum or around 6.2% of the sodium chlorite consumed annually in the US. Accordingly Alcide does not believe that approval for the proposed use will affect current compliance by sodium chlorite producers with environmental regulations.

Use of the food grade acid activators is significantly less, of a larger total commercial utilization, and a similar conclusion is drawn for these materials as well.

Finally, to the best of Alcide Corporation's knowledge and belief, there are no extraordinary circumstances pertaining to the manufacture of the substances (sodium chlorite and food grade organic acids) used in the creation of acidified sodium chlorite.

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7 FATE OF EMITTED SUBSTANCES IN THE ENVIRONMENT

7.1. Introduction

Chorine dioxide (produced from sodium chlorite) is used widely in drinking water treatment in the U.S. When chlorine dioxide reacts in drinking water, approximately 50 - 70% is converted back into chlorite and the remainder into chloride and chlorate. The MCL (Maximum Contaminant Level) for chlorite in drinking water is 1.0 ppm, corresponding to 1.34 ppm sodium chlorite. The Rfd (reference dose) for the chlorate ion is much higher than that for chlorite, and therefore the US EPA (Environmental Protection Agency) has not set a MCL for the chlorate ion. Under The Emergency Planning and Community Right-to-Know Act statute (40 CFR Sect. 313 TRI), the US EPA considers chlorine dioxide releases to the environment at levels below 1.0 ppm to be *de minimis*. Because chlorine dioxide decays rapidly into chlorite, chloride and chlorate, this limit is reflective of the low environmental toxicity of those ions as well.

The chlorite ion is thermodynamically unstable with respect to other chlorine species, e.g., hypochlorite and chloride. It reacts rapidly with Fe(II) and Mn(II) as well as with reduced sulfur species and organic compounds. It is also rapidly degraded photochemically. Consequently, it does not persist in the environment.

In the following, some of the aqueous reactions of the chlorite ion are examined along with its photochemical degradation.

7.2. Chemical Degradation of Chlorite

In acid media, the chlorite ion is in equilibrium with chlorous acid

$$ClO_2^- + H^+ \Leftrightarrow HClO_2 \qquad\qquad pKa = 1.97$$

Below a pH of ~3.5 the following mechanisms predominate

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$$HClO_2 + 3 H^+ + 4 e^- \rightarrow Cl^- + 2 H_2O \qquad 1.57 \text{ V}$$

$$HClO_2 + 2 H^+ + 2 e^- \rightarrow HClO + H_2O \qquad 1.645 V$$
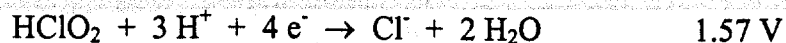
The positive oxidation potentials indicate that the reactions proceed spontaneously as written. The hypochlorous acid, HClO, produced from the second reaction rapidly reacts to produce chloride ion as shown in the following pathway:

$$HOCl + H^+ + 2 e^- \rightarrow Cl^- + H_2O \qquad 1.49 \text{ V}$$
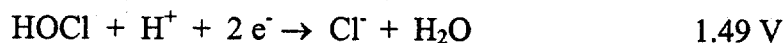
This reaction is much faster than that of hypochlorous acid with organics. Consequently, very few chlorinated organics are formed.

At higher pH values, chlorite can degrade by one or both of the following pathways:

$$ClO_2^- + 2 H_2O + 4 e^- \rightarrow Cl^- + 4 OH^- \qquad 0.76 \text{ V}$$

$$ClO_2^- + H_2O + 2 e^- \rightarrow ClO^- + 2 OH^- \qquad 0.66 \text{ V}$$

Chlorite can also undergo disproportionation reactions (reactions in which two or more molecules of one species react to produce one species with a higher oxidation state along with one of lower oxidation state). This is illustrated in the following reaction in which chlorite/chlorous acid (oxidation state +3) decays into hypochlorous acid (oxidation state +1) and chlorate (oxidation state +5):

$$HClO_2 + ClO_2^- \rightarrow HOCl + ClO_3^-$$
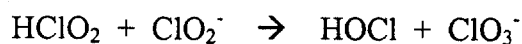
Fabian[17] demonstrated that iron(III) catalyzes the decomposition of chlorite. Iatrou *et al.* [18] investigated the feasibility of using ferrous iron (Fe(II)) to reduce chlorite concentrations. Laboratory tests indicated a required reaction stoichiometry of 3.0 - 3.1 mg Fe(II)/mg ClO_2^-. The

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reaction rate was rapid for pH values of 5 and greater. Interference from dissolved oxygen was minimal. The ferric hydroxide solids produced as a by-product for the Fe(II)-ClO_2^- reaction had no adverse effect on alum coagulation for the removal of turbidity and dissolved organic carbon. Iron catalysis of chlorite is an important degradation pathway in both soils and wastewater streams.

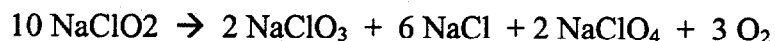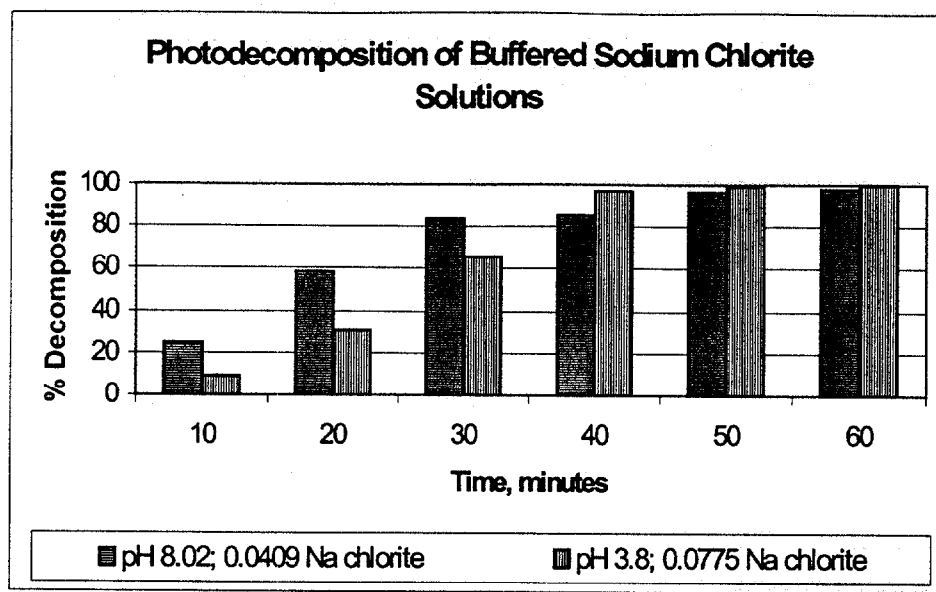## 7.3. Photochemical Degradation of the Chlorite Ion

Buxton and Subhani[19] indicated that the chlorite ion undergoes photolytic decomposition to form chlorate, hypochlorite, chlorine dioxide and oxygen.

The results of work by Cosson et al.[19] suggest that chlorate is not formed by direct photodecomposition of chlorite, but rather by decomposition of chlorine dioxide. Their results are consistent with the stoichiometry

$$3\ ClO_2^- + H_2O + hv \rightarrow Cl^- + 2\ ClO_2 + 2\ OH^- + 0.5\ O_2$$
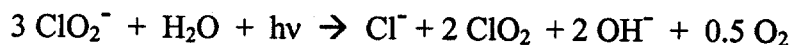
Unless the chlorine dioxide formed from the photolysis of sodium chlorite solutions is removed from solution as soon as it is formed (e.g., via an air sparge) it is rapidly degraded into chlorate and chloride.

In 1964, Nabar et al.[20] published the results of their work on the photodecomposition of chlorite. The following figure shows their results for the fadeometer decomposition of a 0.0409 N $NaClO_2$ solution (3699 ppm) buffered at pH 8.2 and a 0.0775 N $NaClO_2$ solution (7009 ppm) buffered at pH 3.8. The half-life of the higher pH solution was less than 20 minutes; that of the pH 3.8 solution was less than 30 minutes. Decomposition of chlorite solutions by sunlight was reported to be significantly faster. Nabar et al. suggested the following photochemical reaction pathways for the degradation of chlorite under alkaline and acidic conditions, respectively:

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Photodecomposition of Buffered Sodium Chlorite Solutions

Legend: ■ pH 8.02; 0.0409 Na chlorite   ▥ pH 3.8; 0.0775 Na chlorite

$$6\ NaClO_2 \rightarrow 2\ NaClO_3 + 4\ NaCl + 3\ O_2$$

$$10\ NaClO2 \rightarrow 2\ NaClO_3 + 6\ NaCl + 2\ NaClO_4 + 3\ O_2$$

In other work, Zika et al.[21] found that chlorite has a half-life of less than 10 minutes in direct sunlight. More recently, Wang[22] determined that chlorite solutions degraded rapidly (half-life ~ hours) under laboratory fluorescent lighting and even more rapidly in direct sunlight (half-life ~ minutes). This was verified in a field trial at the Los Angeles Country Reservoir[23] in which chlorine dioxide was applied to control algal blooms. Chlorine dioxide was applied at night to give adequate reaction time with the algae present. Within four hours after sunrise, levels of, both chlorine dioxide and its primary degradation byproduct, chlorite, were below detection limits.

7.4. Chlorite Degradation in Soil

In 1999, Certified Laboratories (Plainview, NY) conducted a study (Appendix 2) to simulate the rate of degradation of a spilled chlorite-containing product (Alcide 4XLA Teat Dip, 2400 ppm chlorite acidified with lactic acid to a pH of 3.0). Three different soil samples differing in moisture and

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organic content were used. The results are shown in the following table. It was assumed that in a spill the product would be diluted 1:10. The last column gives the time at which the chlorite level was below the analytical detection limit (~20 ppm in the soils studied).

The rate of degradation was clearly a function of organic loading and also of soil moisture. From these samples, chlorite is not expected to be persistent in soils, and consequently will not have an adverse impact on the environment.

Table 1. Chlorite Degradation in Soil				
Characteristics of Soil Samples				
Sample	Moisture, %	Organics Dry Basis	Organics Soil Basis	Chlorite to "0.0"
A	30.0	13.34	9.34	4 hours
C	3.2	0.72	0.9	8 days
E	44.2	53.07	29.6	8 hours

7.5. Chlorite Degradation in Manure

In another study (Appendix 3), acidified sodium chlorite was added to cow manure at an initial level of 229 ppm. Aliquots were analyzed over a two-day period. The results, in Table 2, show that the chlorite levels had declined approximately 91% (to the 20 ppm detection limit of the method) within 24 hours.

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Table 2. Chlorite Degradation in Manure	
Exposure time (hours)	[Sodium Chlorite] ppm
0	229
0.33	217
0.75	213
1.25	45
4.0	45
5.0	49
15	45
24	20
48	20
Note: Method detection limit was ~20 ppm.	

7.6. Chlorite Degradation in Poultry Processing Waste Waters

Recently, a study was conducted to evaluate the persistence of sodium chlorite in typical poultry processing wastewaters (Appendix 4). Samples of wastewater containing spent ASC (acidified sodium chlorite) treatment solution were collected from four poultry processing plants immediately prior to discharge to the local POTW (publicly owned treatment works), cooled, and shipped to a third-party laboratory for chlorite analysis. Samples were protected from UV exposure during the analytical process.

The following table gives specifics for the four plants where these samples were taken, as well as the calculated chlorite levels in the wastewater. The ASC solution as applied is 1000 ppm sodium chlorite. Typically, 90% of the applied solution goes to drain. The chlorite in this spent solution typically measures 900 ppm.

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Table 3. $NaClO_2$ Concentrations in 4 Poultry Processing Facilities Using ASC					
Plant	Processing Rate Birds/Day	ASC Usage oz/bird	ASC Usage GPD	Total Plant Wastewater MGD	Calculated[†] $[NaClO_2]$ ppm
1	232,050	6 oz	10,877	1.5	5.9
2	156,500	6 oz	7,336	1.5	3.96
3	154,833	6 oz	7,258	1.3	7.64
4	170,260	6 oz	7,981	1.2	5.39
[†]Calculated chlorite in plant effluent = ASC Usage (90% (900 ppm/Total Plant Wastewater					

When the samples were analyzed (Ion Chromatography, EPA Method 300.1), both chlorite and chlorate were not detected, indicating that chlorite is not persistent in the environment.

Furthermore, before discharge into the environment these wastewaters are commingled with other industrial wastewater discharges and domestic wastewaters. Assuming a typical POTW processes 25 MGD, any chlorite from the plants is diluted by a factor of 15-20 (25/1.5 to 25/1.2) using the examples above. The resulting calculated concentration of chlorite contribution to the total effluent entering POTW waters would be well below the 1.0 ppm MCL for drinking water, albeit no degradation occurs.

7.7. Conclusion

Theory predicts, and lab studies and analyses of actual samples (soil, manure, wastewater) confirm, that chlorite decays rapidly in the environment and is not expected to exert any adverse impact.

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8 ENVIRONMENTAL EFFECTS OF RELEASED SUBSTANCES

8.1 EFFECTS ON AQUATIC ORGANISMS

Summaries of relevant portions of this section, as presented in FAP 4A4433 for the oxychlorines that might enter the environment as a result of poultry meat carcass treatment are provided in the next paragraphs. Following the discussion of each specific oxychlorine is a projection of the effects from each of these materials as a result of the treatment of cut surfaces of poultry meat, organs and related poultry parts or trim.

Sodium Chlorite: The LC_{50} aquatic toxicity to fish and oyster species ranged from 41 to 149 ppm, and from 0.151 to 0.650 ppm for *Daphnia magna* and Mysid shrimp, resp. The US-EPA has determined that sodium chlorite is toxic to fish, on the basis of the *Daphnia magna* figure. It was shown in Section 6.2.2.b. that a theoretical maximum level of about 1233 ppb of sodium chlorite would reach the typical POTW. During subsequent waste water treatment or at the POTW, chlorite will mix with other organic laden waters and be rapidly reduced. For effluents that might not be directed to POTWs, but are directed to catch ponds and leaching beds, the high levels of organic matter in the earth environment would rapidly reduce the chlorite to safe levels before the entraining water reached habitable waters for aquatic species.

Sodium Chlorate: The LC_{50} for freshwater and marine fish is consistently >1000 ppm. Sodium chlorate, being a small fraction of the impurities in technical grade sodium chlorite, and forming to only a minor extent during the degradation of ASC solutions, is therefore of no concern from their use in carcass treatments. This conclusion is also directly applicable to the lower volume use of ASC's for treatment of poultry meat parts.

Chlorine Dioxide: The rapidity of degradation of chlorine dioxide in organic environments, coupled with its minimum production in ASC solutions eliminates any aquatic toxicity concerns from carcass treatments. This conclusion is also appropriate for

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effluents resulting from ASC use on poultry meat parts.

8.2. EFFECTS ON TERRESTRIAL ORGANISMS

A summary of the corresponding section in the prior FAP, 4A4433, for poultry carcass processing, is provided in the following paragraphs.

A broad variety of toxicological studies have been carried out on the oxychlorine species chlorite, chlorate and chlorine dioxide, in connection with the worldwide use of chlorine dioxide in the disinfection of potable water. The ClO_2 has been found to produce virtually no chlorinated hydrocarbons as potential mutagens, as does chlorine. On a concentrated basis, the oxychlorines have been found to cause oxidative changes to erythrocytes, both in loss of structural integrity and formation of methemoglobin. However at the ppb levels where these materials may be found in red meat processing plant effluents, be they primary or subprimal and secondary meat grinding operations, the data obtained in connection with drinking water levels of the oxychlorines are more relevant.

On an acute basis, the toxicity of sodium chlorite is in the range of 300 - 350 mg/kg, based on the LD_{50} values for mice, rats, and guinea pigs. For sodium chlorate, the $LD_{50}s$ cover the range of ~600 to 8000 mg/Kg for mice, rats, dogs, cats and rabbits. With respect to the acute toxicity of chlorine dioxide, an LD_{LO} of 500 ppm was found for 15 minutes air exposure by rats. In man, a 5 ppm level in the air was found to be an irritant to the respiratory and G.I. tracts. Such levels would not be found in meat processing plants, either carcass or grinding operations, where any sub-ppm levels of ClO_2 formed during production of the ASC solutions would be rapidly destroyed by organic matter on the carcass or the meat pieces.

A variety of sub-acute studies have been conducted on animals and human volunteers, who ingested waters containing up to 40 ppm of chlorine dioxide in a single episode, or 5 ppm solutions of chlorine dioxide or sodium chlorite for a 12 week period. In the latter case there were some effects on blood chemistry, but little other effects. In the former case there was

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headache, nausea and abdominal discomfort which passed in 5 minutes.

U.S. EPA's recently completed re-assessment of chlorite and chlorine dioxide safety has established a Reference Dose (RfD) for both of these materials of 0.03/mg/kg/day in drinking water, based on an NOAEL (No Observable Adverse Effect Level) of 3 mg/kg/day and a 100-fold safety factor[24]. This corresponds to 2.1 mg/kg/day intake of chlorite or chlorine dioxide for a 70 kg individual. The report of the American Water Works Association's evaluation of chlorite and chlorate residues established a NOEL for chlorate of 78 mg/kg/day, which translates to a maximum intake of 54.6 mg of chlorate per day for a 70 kg person, including the 100 fold safety factor[25].

On the basis of the oxidative tendency of these oxychlorine species to be chemically reduced by organic matter in both the poultry meat treatment, post-washing and plant sanitation waters, and subsequent municipal water treatment facilities, the levels of the three oxychlorine species are anticipated to be significantly lower in waste waters than are the actual levels calculated to be of minimal risk to individuals.

8.3 ENVIRONMENTAL BENEFITS

The use of acidified sodium chlorite acid systems for treatment of meat- and specialty-meat cuts offers the possibility of several environmental benefits:

8.3.1 NON-FORMATION OF MUTAGENS AND CARCINOGENS

In those instances where ASC solutions might be used, or are used in place of chlorinated water for disinfecting meat surfaces (not a common practice), the potential for the formation of chlorinated organic materials in the environment would be significantly reduced.

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8.3.2. REDUCTION IN AQUATIC TOXICITY

Similar considerations would apply to the reduction of hypochlorite in aquatic environments, which has the following toxicity[26]

- Cold water fish: 0.132 – 135 ppm (LC_{50}-96 hr)
- Warm water fish: 0.28 - 2.1 ppm (LC_{50}-96 hr)
- *Daphnia magna*: 0.037 - 2.1 ppm (LC_{50}-48 hr)

These data indicate that chlorine/hypochlorite is much more toxic to both cold and warm freshwater fish than is chlorite or chlorate, and generally slightly more toxic to the *Daphnia magna* invertebrate.

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9 USE OF RESOURCES AND ENERGY

As shown earlier in Section 6, in the worse case scenario, if all of the poultry carcasses slaughtered in the US were to be pre-chill treated with ASC and if all of the post-chill cut surfaces of poultry meat, organs, and related poultry parts or trim were to be similarly treated with ASC, the amount of additional sodium chlorite consumed would be ~30.8% of the total present consumption of sodium chlorite. Inasmuch as the eventual use of ASC solutions in these multiple applications will obviously be significantly less than that maximum (estimated to be around 6.2%), the impact on national resources and energy by such incremental use will be of minimal significance. Also no minerals will be used in the preparation or production of the subject additive. Environmental releases of chlorite, chlorate, chlorine dioxide and any of the GRAS acid activators are not expected to adversely affect threatened or endangered species nor impact historic structures.

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10 MITIGATION MEASURES

No adverse environmental effects are anticipated from residual "worst-case" levels of chlorine dioxide as a result of any aspect of use of the subject additive, if this petition is approved. Therefore, no mitigation measures are required.

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11 ALTERNATIVES TO PROPOSED ACTION

Inasmuch as no potential adverse environmental effects are expected to occur, no mitigation alternative actions are necessary.

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12 PREPARER

This Environmental Assessment was prepared by G. Kere Kemp, Chief Scientific Officer, Alcide Corporation. Dr. Kemp has an educational background in Veterinary Science. His 25 years of work experience have been primarily directed toward the fields of microbiology, pharmacology and pharmacotherapeutics with specific focus on the development and registration of novel and unique antimicrobial substances for potential uses in a variety of animal, human and industrial applications.

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13 CERTIFICATION

The undersigned official certifies that the information presented is true, accurate and complete to the best knowledge of the firm.

Date: _February 1, 2001_

Signature: _____

Name: G. Kere Kemp

Title: Executive Vice President
Chief Scientific Officer

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14 APPENDICES

Appendix 1. Sodium Chlorite Technical Data Sheets and Materials Safety Data Sheets.

Appendix 2. Soria, Y., *Degradation of Chlorite in Soil*. 1999, Certified Laboratories, Inc.: Plainview, NY. p. 81.

Appendix 3. Certified Laboratories, I., *Degradation of Chlorite in Cow Manure*. 1999, Certified Laboratories, Inc.: Plainview, NY. p. 23.

Appendix 4. ABC Research Laboratories,

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